

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
17 May 2001 (17.05.2001)

PCT

(10) International Publication Number
WO 01/34719 A1

- (51) International Patent Classification⁷: C09J 123/16, B42C 9/00
- (72) Inventors: MALCOLM, David, B.; 1200 Willow Lake Boulevard, Box 64683, Saint Paul, MN 55164-0683 (US).
HALLORAN, Kristine, D.; 1200 Willow Lake Boulevard, Box 64683, Saint Paul, MN 55164-0683 (US).
- (21) International Application Number: PCT/US00/30365
- (22) International Filing Date: 3 November 2000 (03.11.2000)
- (74) Agents: QUAN, Nancy, N. et al.; 1200 Willow Lake Boulevard, Box 64683, St. Paul, MN 55164-0683 (US).
- (25) Filing Language: English
- (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- (26) Publication Language: English
- (30) Priority Data: 09/434,172 5 November 1999 (05.11.1999) US
- Published:
— With international search report.
- (71) Applicant: H.B. FULLER LICENSING & FINANCING, INC. [US/US]; 1200 Willow Lake Boulevard, Box 64683, St. Paul, MN 55164-0683 (US).
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 01/34719 A1

(54) Title: HOT MELT ADHESIVES AND METHOD OF USE THEREOF IN BOOKBINDING AT LOW APPLICATION TEMPERATURE

(57) Abstract: The present invention relates to hot melt adhesives and a method of using thereof in bookbinding at low application temperature. More specifically, the invention is directed to hot melt adhesives comprising at least one homogeneous linear or substantially linear ethylene/ α -olefin interpolymers, optionally, at least one block copolymer, at least one tackifying resin, optionally, at least one plasticizer and optionally, at least one additive and/or wax.

HOT MELT ADHESIVES AND METHOD OF USE THEREOF IN BOOKBINDING AT LOW APPLICATION TEMPERATURE

Field Of the Invention

5 The invention relates to hot melt adhesives and method of use thereof in bookbinding at low application temperature. More particularly, the invention relates to hot melt adhesives comprising at least one homogeneous linear or substantially linear ethylene/αolefin interpolmer, optionally, at least one block copolymer, at least one tackifying resin, optionally, at least one plasticizer and optionally, at least one additive
10 and/or wax. Specifically, it relates to a method of using the hot melt adhesives in bookbinding applications such as one shot or perfect bookbinding, two shot bookbinding, casemaking, case-in, gluing-off or thread securing, facing, slip cases, lining up, tightbacking, book joints, side glue, puzzles and gameboard lamination. The hot melt adhesives have low application temperature, long open times, and aggressive bonding
15 properties.

Background Of The Invention

 Hot melt adhesives are applied to a substrate at elevated temperature in a melt form in substantial absence of a solvent. Upon contact with a substrate, the hot melt
20 adhesives solidifies on cooling and forms a strong bond. Hot melt adhesives have been used in bookbinding applications.

 Hot melt bookbinding adhesives are most often based on ethylene vinyl acetate (EVA) copolymers. Other hot melt bookbinding adhesive polymers are polyurethanes and styrenic block copolymers.

25 Block copolymers have been widely used in hot melt adhesives for a variety of applications because of their heat stability, high cohesive strength and compatibility with a wide range of tackifiers and plasticizers. However, the use of many of the polymers in a certain applications is limited because the viscosities of the polymers are too high for processing at a relatively low temperature (less than 350°F).

30 For example, Allen et al., U.S. Patent 4,722,650 discloses the use of A-B-A block or A-B-A-B-A-B multi-block styrene-butadiene copolymer based on hot melt pressure sensitive adhesives for use in case making adhesives for hard cover books.

Flanagan et al., U.S. Patent 4,944,994 relates to the use of radial styrene butadiene block copolymer based hot melt pressure sensitive adhesives for book case making.

Flanagan et al., U.S. Patent 4,660,858 relates to the use of hot melt pressure sensitive adhesive compositions for booklining comprising A-B-A block or A-B-A-B-A-B multi-block copolymer, plasticizing oil, petroleum derived wax and stabilizer.

Beh-Forest et al., U.S. Patent No. 4,712,808 discloses the use of A-B-A block or A-B-A-B-A-B multi-block styrene butadiene copolymer based hot melt adhesives for use in hinge joint applications.

Conventional block copolymers are well known and disclosed in the art of hot melt adhesives. Raykovitz et al., U.S. 4,704,110 relates to hot melt pressure sensitive adhesive composition for use as a positioning adhesive such that the adhesive produces stronger bonds with no adhesive transfer onto the undergarment. The adhesive comprises styrene-butadiene-styrene block or multi-block copolymers, tackifying resin, naphthenic or paraffinic oil and antioxidants.

Collins et al., U.S. Patent No. 4,136,699 disclose hot melt pressure sensitive adhesives for use in absorbent articles comprising two types of A-B-A block copolymers. One type comprises KRATON G, where the A block is polystyrene and the B block is rubbery polyethylene butylene center block. The other type is a teleblock copolymer comprising a molecule having at least three branches radially branching out from a central hub, each of the branches having polystyrene blocks and butadiene segment in the center.

Tse et al., U.S. 5,548,104 disclose hot melt adhesive comprising a blend of ethylene copolymers, tackifiers and wax or oil. While Tse et al., U.S. 5,530,054 disclose a hot melt adhesive comprising ethylene copolymers and a hydrocarbon tackifier, wherein the ethylene copolymer was prepared in the presence of metallocene and alumoxane and having a Mw of from about 20,000 to about 100,000.

There are a variety of uses for hot melt adhesives which are out in the marketplace. However, while one hot melt adhesive may be used for bonding in a particular use or application, the same adhesive may be completely unsuitable for other uses or applications. The present inventors discovered the suitability of the inventive hot melt adhesive composition in bookbinding applications, as well as other applications.

The hot melt adhesives have low application temperature, long open times, and aggressive bonding properties. Moreover, the hot melt adhesives exhibit improved tensile strength in combination with improved heat resistance while maintaining a low molten viscosity.

5

Summary of The Invention

The present invention is directed to a hot melt adhesive composition for use in bookbinding comprising:

- 10 a) at least one homogeneous linear or substantially linear ethylene/ α -olefin interpolpolymer;
- b) optionally, at least one block copolymer;
- c) at least one tackifying resin;
- d) optionally, at least one plasticizer; and
- e) optionally, at least one additive and/or wax.

15 A further aspect of the present invention is directed to a method of binding books, comprising the steps of:

- a) applying a film of a hot melt adhesive to a plurality of sheets at the backbone of a bookblock at a suitable temperature, said adhesive comprising:
 - 20 i) at least one homogeneous linear or substantially linear ethylene/ α -olefin interpolpolymer;
 - ii) optionally, at least one block copolymer;
 - iii) at least one tackifying resin;
 - iv) optionally, at least one plasticizer; and
 - 25 v) optionally, at least one additive and/or wax;
- b) laminating the sheets to the inside of the outer covering of the book; and
- c) allowing the film to solidify.

Another aspect of the present invention is directed to a method for lining hard bound book blocks comprising the steps of:

- 30 a) applying a molten film of hot melt adhesive to the bound edges of a book block;
- b) applying thereto a scrim;

- c) applying a second molten film of hot melt adhesive; and
- d) affixing thereto a strip of kraft paper in registered relation to the book spine; said hot melt adhesive comprising:
 - i) at least one homogeneous linear or substantially linear ethylene/ α -olefin interpolymer;
 - ii) optionally, at least one block copolymer;
 - iii) at least one tackifying resin; and
 - iv) optionally, at least one plasticizer;
 - v) optionally, at least one additive and/or wax.

Still another aspect of the invention is directed to a method for lining hard bound books blocks comprising the steps of:

- a) applying a molten film of hot melt adhesive to the bound edges of a book block;
- b) optionally, applying capping paper over the molten hot melt adhesive;
- c) applying a second molten film of hot melt adhesive;
- d) applying thereto a scrim;
- e) applying a third molten film of hot melt adhesive; and
- f) affixing a strip of kraft paper in registered relation to the book spine.

A further aspect of the present invention relates to a method of using a hot melt adhesive for casemaking comprising the steps of:

- a) applying a hot melt adhesive to the book outer covering material;
- b) placing book binder boards onto the outer covering material; and
- c) laminating the outer covering material to the binder boards.

Another aspect of the present invention relates to a method of using a hot melt adhesive for casing-in comprising the steps of:

- a) applying a hot melt adhesive to the end sheets of a book block; and
- b) laminating the end sheets to the inside of the book cover.

A further aspect of the present invention relates to a method of using a hot melt adhesive for gluing-off or thread-securing, comprising the steps of:

- a) sewing a book or booklet together through the spine of the book or booklet using thread;

- 5
- b) extruding the hot melt adhesive onto the spine of the book or booklet substantially covering the threads; and
 - c) applying the book or booklet case to the spine of the book or booklet; wherein the hot melt adhesive is between the case and the spine of the book or booklet.

Still another aspect of the present invention relates to a case or cover for hard bound book comprising:

- 10
- a) an outer covering material; and
 - b) book binder boards wherein the binder boards are bonded to the outer cover material with the hot melt adhesive.

A further aspect of the present invention relates to a book comprising:

- 15
- a) a book block comprising a plurality of sheets; and
 - b) a book cover or case bonded to the end sheets of the book block with the hot melt adhesive.

Another aspect of the present invention relates to a sewn book or booklet comprising:

- 20
- a) threads sewn through the spine of the book or booklet;
 - b) a hot melt adhesive extruded onto the spine; and
 - c) a case bonded to the spine with the adhesive.

A further aspect of the present invention relates to a hot melt adhesive composition according to the present invention comprising:

- 25
- a) from about 5 to about 50-wt-% of at least one homogeneous linear or substantially linear ethylene/ α -olefin interpolymers;
 - b) optionally, from about 5 to about 50 wt-% of at least one block copolymer;
 - c) from about 30 to about 80 wt-% of at least one tackifying resin;
 - d) optionally, from about 5 to about 55-wt% of at least one plasticizer; and
 - e) from about 0 to about 50 wt-% of at least one additive and/or wax.

30 Other aspects, objects, features and advantages of the present invention would be apparent to one of ordinary skill in the art from the following detailed description illustrating the preferred embodiments of the invention.

Detailed Description Of The Invention

The following glossary is provided as an aid to understand the use of certain terms herein. The explanation provided in the glossary are for illustrative purposes and
5 do not limit the scope of the invention.

For purposes of the invention, the word "bookbinding" will be used to describe the process by which books are produced. However, this invention is not limited to adhesives suitable for binding only books. As used herein, the term "books" is intended to include articles containing pages bound with an adhesive including but not limited to
10 paperback books, pamphlets, laboratory notebooks, soft cover books, instruction manual magazines, catalogs, trade journals, directories and the like.

In the bookbinding process, there are two distinctly different processes, namely, "perfect binding" and "traditional" bookbinding. In a traditional bookbinding, hard bound books consist of two main components, namely the case and the body. The case
15 comprises the front and back covers connected by the spine. The body of the book, also known as "block" is comprised of a plurality of paper sheets or leaves which are generally sewn together along their center folds in groups to form the sections or "signatures" of the book. The signatures are then assembled to form the body of the book. The front and back of the body are affixed heavy folded pages, called "end
20 papers" which facilitates the attachment or "casing in" of the body to the case. The adhesives are employed in several ways. One process is referred to as "gluing off" wherein the adhesive is rollcoated or extruded onto the spine of the book, in addition to the thread or wire used to bind and seal pages of the book together. In another process referred to as a "lining", the adhesive is used to attach a reinforcing material such as
25 cloth or paper to the book spine. Another process is referred to as "casing in" or attachment process wherein the adhesive is used to attach the book cover to the book spine.

In a "perfect binding", the adhesive alone is used to bind the pages of the book together and to attach the book's cover. If only one adhesive is used to construct the
30 book, it is called a "one shot process". When two adhesives are used, it is called a "two shot process". In a two shot process, the first application of the adhesive is referred to as

a primer glue. The second application is used to attach the book's cover to the book spine. The adhesive is referred to as a "cover glue".

In a "perfect binding" technique, the pages are printed in long, continuous sheets or webs which are cut, folded and properly arranged to form a series of stacks called "signatures". The signatures are then fed into a continuous, revolving chain equipped with clamps. The free edges of the clamped sheets are first cut to remove the signature folds. It is then roughed to expose a maximum amount of fibers at the edges of the sheets and to make them more receptive to the adhesive composition. A layer or coat of a hot melt adhesive composition is then applied in a molten form by means of suitable applicator. The end papers are applied before the molten adhesive sets to form the spine of the book.

A third process for the production of book block involves the burst, perforate or notched method where the book block maintains the signature fold but contains burst, perforations or notches into the innermost page of the signature and wherein the adhesive is applied to the burst, perforate or notched signature to form the book block.

After the book block is formed, the next step in the manufacture of books is rounding or backing if the book is intended to have a curved or rounded configuration. After the rounding, the next process is referred to as "lining", where a reinforcing material called a "super" or "crash" is applied to the spine or backbone of the book. This is done by gluing the center of the gauze like scrim "super" or "crash" to the book block or spine. The ends of the scrim extends about 7/8 inch along the outside of the end papers on either side of the body. After the scrim or super is applied, a second coat of the adhesive is typically applied and a kraft strip with an optional headband is applied. A second or third adhesive coating step is not required if sufficient adhesive is applied in gluing of the scrim in order to penetrate the scrim. The application of the kraft backing which is in registered relation to the book spine, optional headbands and the scrim combine to form the traditional lining for the book.

The "super" or "crash" is applied over capping paper but it can be applied directly to the hot melt binding adhesive. It is in this heat of application, where the softening of the underlying hot melt film, and subsequent trapping of the heat after combination with the cover, that the loss of adhesion and poor book strength may result. Alternatively, if the heat of application is unable to be effectively conducted away or

otherwise cooled, it results in a very slow setting characteristics. This in turn can result in delamination or damage to the book during stacking or handling of the book prior to the complete setting of the hot melt adhesive films comprising the backbone. A wide ambient temperature range characterizes the hot melt adhesives of the present invention
5 considering that a rather low viscosity is required for the low application temperature.

The lined book block is inserted into the case such that the folds in the end papers are adjacent the spine of the case. The adhesive is applied to the front and back end papers adjacent the inside covers of the case. The end papers are pasted to the inside of covers, enclosing the crash. The case and body are then passed through a "building in"
10 operation to form a groove at either edge of the case spine or placed in a press. When the attachment process, termed as "casing in" is complete, the body is bound to the cover incorporating a hinge so that the covers and leaves are movable with respect to each other.

"Casing in" refers to the process wherein the book block is bonded to the inside
15 cover of a "hard" bound book. "Casing in" is accomplished by coating the outside of the end sheets of the book block with adhesive and then laminating the end sheets to the inside of the cover of the book or by coating the inside of the case or cover and then laminating the end sheets of the book block to it. The application of the adhesive to the outside edges is accomplished generally by a Stahl or Kolbus using a water based
20 adhesive. Alternatively, a hot melt adhesive can be applied by modifying the equipment such as by using a heated reservoir.

The hot melt adhesive is also applied to the book joint which is the recessed area between the cover and the back of the book, for example the lateral edges or outside of the bookblock in hard books.

25 Tightbacking application is wherein a strip of kraft paper is applied over a composite which is the backlining adhesive, and hot melt adhesive is applied over the kraft paper in the backlining. The backlining area is bonded to the cover of the bookblock.

Casemaking is a method by which a case or cover for a hard bound book is
30 formed. In this method, the material that forms the outer covering of a book is bonded by the use of adhesives to binder boards which are usually chipboards to form actual "hard" covers of books. The material used for the outer covering may include but are not

limited to cloth, leather, paper, vinyl, polyethylene and composite materials such as cloth or paper laminated to polyethylene, polyester or mylar and polypropylene. Many other materials known to one of ordinary skill in the art are also useful for making book covers.

- 5 The covering material may either be in precut form or continuous web form depending on the type of application equipment which is used. The covering material is passed along a conveyor during which time the binder boards which are usually precut are mated onto the adhesive coated covering material. If the binder boards are precut in two pieces, then a center strip is usually laid down where the backbone of the book is
- 10 formed. If the covering material is not precut, it will be cut at this point so that it extends up to about 1 inch beyond the perimeter of the binder board. The surplus covering material is then folded over the binder board in a two step process also known as "turning in". Turning in is a process in which either the sides are folded in first and the ends are folded in a second resulting in an overlap of the ends over the sides or the ends
- 15 are folded in first and the sides are folded in second. These are called "turn ins".

- Several important performance properties of books include page-pull, lay-flat, page-flex, cold crack, easy-open and spine-flexibility. Lay-flat refers to a characteristic of a book to remain open at a given page and how flat it lies (spine up or down). Page-pull refers to the force required to pull an individual page from a bound book. Page-pull
- 20 depends upon both the adhesive and the surface preparation of the book block. Page-flex is a complex function of the adhesive characteristics, penetration of the adhesive into book block, surface preparation of the book block. Cold crack refers to the temperature at which the spine of a book will crack when it is quickly opened so that it covers touch. Easy-open refers to the amount of resistance a book offers when it is first opened. Spine-
- 25 flexibility refers to the ability of the book to be opened repeatedly without the spine creasing or wrinkling. The properties such as Lay-flat, Cold crack, Easy-open and spine-flexibility depend upon the adhesive characteristics and amount of the adhesive applied.

- "Open time" refers to the time during which a bond may be formed. In the application of hot melt adhesives, it is highly desirable for the hot melt adhesives when
- 30 molten to remain capable of sticking for a relatively long period of time to enable materials to be bonded to be correctly positioned. Thus, the open time available from applying the molten hot melt adhesives to substrate to be bonded until all substrates are

brought together should be long. In contrast, the "setting time" which is the time from bringing the substrates together until bond is set should be short.

The adhesive composition of the invention comprises at least one homogeneous linear or substantially linear ethylene/ α -olefin interpolmer which is an interpolmer of
5 ethylene and at least one C_3 - C_{20} α -olefin. The term "interpolymer" as used herein indicates a copolymer, or a terpolymer or a higher order polymer. That is, at least one other comonomer is polymerized with ethylene to make the interpolmer.

By the term "homogeneous", it is meant that any comonomer is randomly distributed within a given interpolmer molecule and substantially all of the interpolmer
10 molecules have the same ethylene/comonomer ratio within that interpolmer.

The term "substantially linear polymers" means the polymer backbone is substituted with about 0.0 long chain branches/1000 carbons to about 3 long chain branches/1000 carbons, more preferably from about 0.01 long chain branches/1000 carbons to about 1 long chain branches/1000 carbons and most preferably, 0.05 long
15 chain branches/1000 carbons to about 1 long chain branches/1000 carbon.

The term "linear ethylene polymers" means that the ethylenic polymer does not have long chain branching. The linear ethylenic polymer has an absence of long chain branching, as for example, the conventional linear low density polyethylene polymers or linear high density polyethylene polymers made by using Ziegler polymerization
20 processes. See for example, U.S. Patents 4,076,698 or 3,645,992, the disclosures of which are incorporated herein by reference.

Long chain branching refers to a chain length of at least about 6 carbons, above which can not be distinguished using ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The long chain branching can be as long as about the same length as the
25 length of the polymer backbone. Methods for determining the amount of long chain branching present, both quantitatively and qualitatively are known in the art. The qualitative determination of long chain branching is disclosed in U.S. Patent Nos. 5,272,236 and 5,278,272. The long chain branching is determined by ^{13}C NMR spectroscopy and is quantified using the method of Randall, Rev. Macromol. Chem.
30 Phys., C29 (2&3), pp.285-297, the disclosures of which are incorporated herein by reference.

The invention is directed to a hot melt adhesive composition comprising at least one homogeneous ethylene/ α -olefin interpolymers which is an interpolymers of ethylene and at least one C_3 - C_{20} α -olefin, at least one block copolymer, at least one tackifying resin, optionally, at least one plasticizer and optionally, at least one additive and/or wax.

5 The concentration of the homogeneous ethylene/ α -olefin interpolymers is preferably from about 5 wt-% to about 40 wt-%, whereas the concentration of the block copolymer ranges from about 1 wt-% to about 40 wt-% more preferably from about 10 wt-% to about 20 wt-%. In the case of pressure sensitive adhesives, at least one tackifying resin and a plasticizer are preferred whereas for non-pressure sensitive
10 adhesive compositions, at least one tackifying resin and at least one wax is preferred. The tackifying resin is employed at a concentration of at least about 30 wt-%.

 The homogeneous ethylene/ α -olefin interpolymers preferably has a density ranging from 0.850 to about 0.885 g/cm³. To minimize the molten viscosity of the adhesive composition, the homogeneous ethylene/ α -olefin interpolymers preferably has a
15 melt index of greater than about 10 grams/10 minutes, more preferably greater than about 30 g/ 10 min, even more preferably greater than about 100 g/ 10 min, and most preferably greater than about 500 g/10 minutes.

 Homogeneous ethylene/ α -olefin interpolymers differ from amorphous polyolefins also described as amorphous polyalphaolefins (APAO), with regard to
20 homogeneity, molecular weight distribution (Mw/Mn), as well as comonomer (α -olefin) content. Amorphous polyolefins are homopolymers, copolymers and terpolymers of C_2 - C_8 , α -olefin which are typically polymerized by means of processes which employ Ziegler-Natta catalysts, resulting in a relatively broad molecule weight distribution, typically greater than 4. In contrast, the homogeneous ethylene/ α -olefin interpolymers
25 useful in the inventive adhesive composition are characterized as having a narrow molecular weight distribution. The homogeneous ethylene/ α -olefin have a Mw/Mn of less than 4, preferably less than 3, more preferably from 1.5 to 2.5, even more preferably from 1.8 to 2.2, and most preferably about 2.0. Further, whereas amorphous polyolefins are produced from Ziegler Natta catalysis typically have an α -olefin concentration
30 greater than 50 wt-%, homogeneous ethylene/ α -olefin interpolymers useful in the present invention are predominately ethylene, having a greater ethylene content than the comonomer content.

It is also noted that substantially linear interpolymers useful in the invention differ from low density polyethylene prepared in a high pressure process. In one regard, whereas low density polyethylene is an ethylene homopolymer having a density of from 0.900 to 0.935 g/cm³, the homogeneous linear and substantially linear ethylene/ α -
5 interpolymers useful in the invention require the presence of a comonomer to reduce the density.

The homogeneous ethylene/ α -olefin interpolymers are a homogeneous linear or substantially linear ethylene/ α -olefin interpolymers. The melting peak of homogeneous linear and substantially linear ethylene polymers, as obtained using differential scanning
10 calorimetry will broaden as the density decreases and/or as the number average molecular weight decreases. However, unlike heterogeneous polymers, when a homogeneous polymer, prepared in a solution polymerization process, has a melting peak greater than 115 °C (such as is the case of polymers having a density greater than 0.940 g/cm³), it does not additionally have a distinct lower temperature melting peak.

15 Substantially linear ethylene interpolymers are homogeneous interpolymers having long chain branching. Due to the presence of such long chain branching, substantially linear ethylene interpolymers are further characterized as having a melt flow ratio (I_{10}/I_2) which may be varied independently of the polydispersity index, and the like, the molecular weight distribution M_w/M_n . This feature accords substantially linear
20 ethylene polymers with a high degree of processability despite a narrow molecular weight distribution.

The long chain branches of substantially linear ethylene interpolymers have the same comonomer distribution as the interpolymers backbone and can be as long as about the same length as the length of the interpolymers backbone. When a substantially linear
25 ethylene/ α -olefin interpolymers is employed in the practice of the invention, such interpolymers will be characterized as having an interpolymers backbone substituted with from 0.01 to 3 long chain branches per 1000 carbons.

The homogeneous ethylene/ α -olefin interpolymers are an interpolymers of ethylene with at least one comonomer selected from the group consisting of C₃-C₂₀ α -olefins, non-
30 conjugated dienes, and cycloalkenes. Exemplary C₃-C₂₀ α -olefins include propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, and 1-octene. Preferred C₃-C₂₀ α -olefins include 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, and 1-

- octene, more preferably 1-hexene and 1-octene. Exemplary cycloalkenes include cyclopentene, cyclohexene and cyclooctene. The non-conjugated dienes suitable as comonomers, particularly in the making of ethylene/ α -olefin/diene terpolymers, are typically non-conjugated dienes having from 6 to 15 carbon atoms. Representative
- 5 examples of suitable non-conjugated dienes include:
- (a) Straight chain acyclic dienes such as 1,4 hexadiene; 5-heptadiene; and 1,6-octadiene;
 - (b) Branched chain acyclic dienes such as 5-methyl-1, 4-hexadiene; 3,7-dimethyl-1,6-octadiene; and 3,7-dimethyl-1,7-octadiene;
 - 10 (c) Single ring alicyclic dienes such as 4-vinyl cyclohexene; 1-allyl-4-isopropylidene cyclohexane; 3-allyl cyclopentene; 4-allyl cyclohexene; and 1-isopropenyl-4-butenylcyclohexene;
 - (d) Multi-ring alicyclic fused and bridged ring dienes such as dicyclopentadiene; alkenyl, alkylidene, cycloalkenyl, and cycloalkylidene norbornenes, such as 5-
 - 15 methylene-2-norbornene; 5-methylene-6-methyl-2-norbornene; 5-methylene-6,6-dimethyl-2-norbornene; 5-propenyl-2norbornene; 5-(3-cyclopentenyl)-2-norbornene; 5 ethylidene-2-norbornene; and 5-cyclohexylidene-2-norbornene.

One preferred conjugated diene is piperylene. The preferred dienes are selected from the group consisting of 1,4-hexadiene; dicyclopentadiene; 5-ethylidene-2-

20 norbornene; 5-methylene-2-norbornene; 7-methyl-1,6 octadiene; piperylene; and 4-vinyl cyclohexene.

The molecular weight of the homogeneous ethylene/ α -olefin interpolymer will be selected on the basis of the desired performance attributes of the adhesive formulation. Typically, the homogeneous ethylene/ α -olefin interpolymer will have a number average

25 molecular weight of at least 800 grams/mole, preferably at least 1,300 and no more than 100,000 grams/mole. Ultra meolecular wieght homogeneous ethylene/ α -olefin interpolymer are considered to have a number average molecule weight of less than about 11,000 g/mole.

For adhesive applications in which high viscosity compositions are

30 unproblematic, homogeneous ethylene/ α -olefin interpolymers having a melt index as low as 0.25 g/10 min. may be employed. However, for the majority of hot melt adhesive applications, wherein it is desired to minimize viscosity, the homogeneous ethylene/ α -

olefin interpolymers typically have a melt index greater than about 10 g/10 min., more typically greater than 20 g/10 min., preferably greater than about 30 g/10 min., more preferably, greater than about 50 g/10 min., even more preferably greater than about 50 g/10 min., even more preferably greater than about 100 g/10 min., even more preferably greater than about 200 g/10 min. and most preferably the melt index ranges from about 500 g/10 min. to about 2500 g/10 min. Further, in some instances, the melt index can range as high as 4000 g/10 min.

The melt index inversely relates to the molten viscosity. The viscosity at 350°F (177°C) ranges from about 2,000 cPs to about 2,000,000 cPs, preferably from about 3,500 cPs to about 1,000,000 cPs, and more preferably from about 5,000 cPs to about 100,000 cPs.

The density of homogeneous ethylene/ α -olefin interpolymers will be selected on basis of desired performance attributes of the adhesive formulation. Typically however, the homogeneous ethylene/ α -olefin interpolymers will have a density of at least 0.850 g/cm³, preferably at least 0.860 g/cm³, and more preferably about 0.870 g/cm³. For the majority of the preferred compositions for targeted adhesive applications, the homogeneous ethylene/ α -olefin interpolymers will have a density of no more than 0.965 g/cm³, preferably no more than 0.900 g/cm³, more preferably no more than 0.890 g/cm³, and even more preferably no more than 0.885 g/cm³, and most preferably no more than 0.880 g/cm³.

The homogeneous ethylene/ α -olefin interpolymers will be present in the adhesive composition of invention in an amount greater than about 5 wt-%, and preferably greater than about 10 wt-%. The homogeneous ethylene/ α -olefin interpolymers will typically be present in the adhesive of the invention in an amount less than about 50 wt-%, preferably less than about 40 wt-%, and more preferably less than about 30 wt-%.

The adhesive composition comprises either a single homogeneous ethylene/ α -olefin interpolymers or a blend of two or more interpolymers. In instances where a single homogeneous ethylene/ α -olefin interpolymers is employed, the interpolymers will preferably have a density ranging from about 0.850 g/cm³ to 0.995 g/cm³ and a melt index of greater than about 100 g/10 min. In the case of homogeneous ethylene/ α -olefin interpolymers blends, the density of the interpolymers blend will preferably possess the

targeted density, and melt index. However, the individual interpolymers comprising the blend may have a density and/or melt index outside of the specified range.

When employing two or more homogenous ethylene/ α -olefin interpolymers, the first and second interpolymer will differ from each other with respect to the type of comonomer and/or the molecular weight or melt index, and/or the density, and/or the molecular weight distribution. Accordingly, the first and second interpolymer may differ in number average molecular weight by at least 5000, preferably at least 10,000, and more preferably at least 20,000. In addition or in the alternative, the first and second interpolymers differ in density by at least 0.005 g/cm³, preferably by at least 0.01 g/cm³.

Homogeneously branched linear ethylene/ α -olefin interpolymers may be prepared using polymerization processes (for example, as described by Elston, U.S. Patent No. 3,645,992, the disclosures of which are incorporated herein by reference), which provide a homogeneous short chain branching distribution. In his polymerization process, Elston uses soluble vanadium catalyst systems to make such polymers. However, others such as Mitsui Petrochemical Company and Exxon Chemical Co have used the so-called single site catalyst systems to make polymers having homogeneous linear structure. U.S. Patent No. 4,937,299 to Ewen et al. And U.S. Patent No. 5,218,071 to Tsutsui et al. Disclose the use of catalyst systems based on hafnium for preparation of homogeneous linear ethylene polymers. Homogeneous ethylene/ α -olefin interpolymer are currently available from Mitsui Petrochemical Company under the trade name "Tafmer®" and from Exxon Chemical Company under the trade name of Exact®.

Substantially linear ethylene/ α -olefin interpolymers are available from the Dow Chemical Company as Affinity® polyolefin plastomers and Engage® polyolefin elastomer. Substantially linear ethylene/ α -olefin interpolymers may be prepared in accordance with the techniques described in Lai et al., U.S. Patent No. 5,272,236 and in U.S. Patent No. 5,278,272, the disclosures of which are incorporated herein by reference.

Ultra-low molecular weight polymers may also be suitably prepared using a constrained geometry metal complex, according to the procedures of U.S. Serial No. 08/784,683, herein incorporated by reference in its entirety.

A wide variety of block copolymers are useful in the present invention including A-B-A triblock structures, A-B di-block structures, (A-B)_n radial block copolymer structures, as well as branched and grafted versions of such structures wherein the A

endblock is a non-elastomeric polymer block, typically comprising polystyrene and/or vinyl, and the B block is typically ethylene/butylene (hydrogenated butadiene), ethylene/propylene (hydrogenated isoprene), isoprene, butadiene (which is partially or substantially hydrogenated as taught in Wald et al., U.S. 3,700,633) and mixtures thereof. The conditions are necessary to hydrogenate the elastomeric butadiene while not modifying the styrene polymer block. Other conditions may be chosen to hydrogenate substantially uniformly along the polymer chain, both elastomeric and non-elastomeric blocks thereof being hydrogenated to practically the same extent which may be partial or substantially complete. Further, they may be linear or branched. Typical branched structures contain elastomeric branched structure contain an elastomeric portion with at least three branches which can radiate out from a central hub or can otherwise be coupled together.

Typical of the rubbery copolymers useful therein are polystyrene-polybutadiene-polystyrene and polystyrene-poly(ethylenebutylene)-polystyrene. These copolymers may be prepared using the methods taught for example in Harlan, U.S. Patent Nos. 3,239,478; Davis, U.S. Patent No. 3,427,269; Wald et al., U.S. Patent No. 3,700,633; Mars, U.S. Patent No. 3,753,936; and Naylor, U.S. Patent No. 3,932,327. Alternatively, KRATON® 1101, 1102, 1650, 1652 and 1657 are commercially available from Shell Chemical Company. Similar copolymers are commercially available from Phillips Chemical Company under the tradename Solprene® 418 and 423. Commercially available block copolymers useful for the invention include KRATON® G-1650, a 29% styrene, 8000 solution viscosity (25 wt-% polymer), 100% triblock styrene-ethylene-butylene-styrene (S-EB-S) block copolymer; KRATON® G-1652, a 29% styrene, 1350 solution viscosity (25 wt-% polymer), 100% triblock S-EB-S block copolymer; KRATON® G-1657, a 4200 solution viscosity (25 wt-% polymer), 35% diblock S-EB-S block copolymer; all available from the shell Chemical Company. The preferred block copolymers are of the styrene-ethylene/propylene (S-EP) types and are commercially available under the tradenames KRATON® G-1726, a 28% styrene, 200 solution viscosity (25 wt-% polymer), 70% diblock S-EB-S block copolymer; KRATON® G-1701X a 37% styrene, >50,000 solution viscosity, 100% diblock S-EP block copolymer; and KRATON® G-1702X, a 28% styrene, >50,000 solution viscosity, 100% diblock S-

EP block copolymer, KRATON® G-1730, a 22% styrene, (SEPS) block copolymer also available from The Shell Chemical Company.

Preferably, the block copolymer has styrenic end block(s) and a midblock comprising ethylene/butylene, ethylene propylene, and mixtures thereof. Most preferred
5 block copolymers have a solution viscosity of at least 50 cPs or greater, more preferably about 100 cPs, and most preferably about 200 cPs up to about 2000 cPs for 25 wt-% solution of the polymer in toluene at 25°C and a diblock content of greater than about 35 wt-%, more preferably greater than about 50 wt-%, and most preferably ranging from about 70 wt-% to about 100 wt-% diblock.

10 In order to achieve the preferred viscosity and ring and ball softening point, preferably the block copolymer has a melt index of greater than about 10 g/10 min, more preferably greater than about 20 g/10 min., even more preferably greater than about 30 g/10 min., and most preferably ranging from about 50 g/10 min., to 200 g/10 min. Additionally, in order to achieve the required softness or deformability, higher diblock
15 containing polymer are preferred alone or in combination with a predominately triblock, 100% coupled, block copolymer structure. Diblock refers to the molecules having an A-B structure wherein A is a nonelastomer such as polystyrene and B is the rubbery block. Diblock differs from triblock in that it does not have a nonelastomeric styrene or vinyl blocks on both ends. Preferably, the diblock content of the block copolymer(s) is greater
20 than about 35 wt-% with respect to the total weight of the block copolymers, more preferably about 50 wt-% and greater, and more preferably about 70 wt-% to about 100 wt-% diblock. Further, preferred block-copolymers have an endblock to midblock ratio of 10/90 (10% styrene end block) to 40/60 wt-% and more preferably ranging from about 25 wt-% to about 40 wt-% endblock (styrene). The molecular weight of the block
25 copolymer is about 50,000 to about 150,000, preferably about 50,000 to about 130,000. The block copolymer has a styrene content of about 15 wt% to about 30 wt-% styrene, preferably about 20 wt-% styrene.

The adhesive of the present invention comprises optionally at least one block copolymer present in an amount ranging from about 0.5 wt-% to about 30 wt-%,
30 preferably from about 2 wt-% to about 25 wt-% and more preferably about 3 wt-% to about 20 wt-%. At a concentration of 1 wt-%, the effect is subtle but detectable. At a concentration below 1 wt-%, the effect of the block copolymer tends to be subtle that is

difficult to detect with most adhesive performance testing. At concentrations greater than about 30 wt-%, the viscosity tends to be too high for the majority of adhesive applications. Further, minimal block copolymer concentrations tend to be advantageous with respect to cost.

- 5 The adhesive of the present invention comprises at least one tackifying resin present in an amount ranging from about 30 wt-% to about 80 wt-%, preferably from about 35 wt-% to about 65 wt-%, more preferably from about 40 wt-% to about 60 wt-%, and most preferably from about 40 wt-% to about 45 wt-%.

- Examples of tackifying resins may include: a) natural and modified rosins such as
10 gum rosin, wood rosin, tall oil rosin, distilled rosin, hydrogenated rosin, dimerized rosin and polymerized rosin; b) glycerol and pentaerythritol esters of natural and modified rosins such as glycerol ester of pale, wood rosin, the glycerol ester of polymerized rosin, pentaerythritol esters of hydrogenated rosin and phenolic modified pentaerythritol esters of rosin; c) copolymers and terpolymers of natured terpene such as styrene/terpene,
15 linear homopolymers of α -methyl styrene, α -methyl styrene copolymer resin; d) polyterpene resins having a softening point as determined by ASTM method E28-58T of from 80° to 150°C; the latter polyterpene resins generally resulting from the polymerization of terpene hydrocarbons such as bicyclic monoterpene known as pinene in the presence of Friedel Craft catalysts at moderately low temperature; also included are
20 hydrogenated polyterpene resins; e) phenolic modified terpene resins and hydrogenated derivatives thereof such as the resin product resulting from the condensation in an acidic medium of a bicyclic terpene and a phenol; f) aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from 70° to 135°C, the latter resins resulting from the polymerization of monomers consisting of primarily of olefins and diolefins;
25 also included are hydrogenated aliphatic petroleum hydrocarbon resins; g) aromatic petroleum hydrocarbon resins and hydrogenated derivatives thereof; h) alicyclic petroleum hydrocarbon resins and hydrogenated derivatives thereof. Mixtures of two or more of the above described tackifiers may be required for some formulations. Preferred tackifying resins include hydrogenated rosins, hydrogenated polyterpene resins and
30 aliphatic petroleum hydrocarbon resins.

 However, higher tackifying resin concentrations may be employed if tackifying resin is a liquid at ambient temperature (25°C). The tackifying resins useful to the

present invention are also substantially saturated and included dicyclopentadiene based resins, substantially fully hydrogenated aliphatic C₅ and C₉ resins, and substantially saturated aromatic monomer based resins such as α -methylstyrene based resins.

Commercially available tackifying resins suitable for use in the present invention include
5 Arkon® P 90, Arkon® P 125 Arkon® P 140, fully saturated alicyclic hydrocarbon resins from the Arakawa Chemicals Industries Ltd.; ESCOREZ® 5300, ESCOREZ® 5320, ESCOREZ® 5340 and ESCOREZ® 5380, dicyclopentadiene resins from Exxon Chemical Company; Regalrez® 1018, a liquid resin (T_g = -20°C) based on hydrogenated polymerized styrenic based monomers; as well as KRISTALEX® F85 and
10 KRISTALEX® F100, α -methyl styrene resins from Hercules GmbH. Tackifying resins which are also surmised to be useful such as the ESCOREZ® 5400 series as well as Hercules REGALITE® R-type resins.

Polyterpene resins have been blended with waxes and polymers to make hot melt adhesives as disclosed in the bulletin entitled "ESCOREZ® 5000 Resins for Hot Melt
15 Adhesives" published by Exxon Chemical Company. The bulletin discloses formulations which include wax, ethylene vinyl acetate copolymer and resin.

The hot melt adhesive of the present invention comprises a plasticizer or extending agent present in an amount ranging from about 5 wt-% to about 55 wt-%, preferably from about 15 wt-% to about 35 wt-% and most preferably from about 20 wt-
20 % to about 30 wt-%.

Plasticizing diluents may include predominatly paraffinic oils having minor amounts of naphthenic and minor amounts of aromatic components as well as liquid polymers such as low softening point α -olefins, particularly polyisobutylene and liquid copolymers such as LSVI®-101. Preferably, the plasticizing diluent is an oil which
25 comprises a paraffinic content of 50 wt-% to 90 wt-%, a naphthenic content of about 10 wt-% to about 40 wt-% and an aromatic content of no more than about 10 wt-% such as white mineral oils. Such oils are commercially available under the trademarks CATENEX®, e.g., CATENEX® P941 of the Shell Company or Shell Oil® 4142 FU, Shellflex® 371 made by Shell Chemical Company, as well as Kaydol® oil of the Witco
30 Company and Tuflo® oil made by Mobil Chemical Company.

Suitable plasticizers include hydroxylated benzoates or acetates or benzoates of polyols such as acetate or benzoates of C₂-C₆ comprising 2-6 hydroxyl groups.

Plasticizers include acetin, glyceryl diacetate, 1,4 cyclohexane dimethanol dibenzoate (Benzoflex® 352) glyceryl tribenzoate (Benzoflex® S-404), pentaerythritol tetrabenzoates (Benzoflex® S-552) or mixed dibenzoates of dipropylene glycol and diethylene glycol (Benzoflex® 50) which are commercially available from Velsicol Corp., Chicago, IL. Other plasticizers such as butyl benzyl benzoate are commercially available from Monsanto as Santicizer® 160 and Dicyclohexyl phthalate (Morflex® 150), commercially available from Morflex Inc., Greensboro, NC.

Various petroleum derived waxes may also be added in amounts of more than about 15% by weight of the composition in order to impart fluidity in the molten condition of the adhesive and flexibility to set the adhesive and to serve as a wetting agent. The term "petroleum derived wax" refers to paraffin and microcrystalline waxes having melting points within the range of about 130° to 225°C until a homogeneous blend is obtained. Waxes useful in the adhesives of the present invention include paraffin waxes, microcrystalline waxes, Fischer-Tropsch, polyethylene and by-products of polyethylene wherein the MW is less than 3,000. A preferred wax is paraffin wax. Paraffin waxes such as Shellwax® 200, 300 and 650 and Shellwax® 400 and 500 are commercially available from Shell Chemical Company. Other Wax extenders include BE® 175 and 195 made by Petrolite, and Epolene® C-10 and C-17 made by Eastman Chemical Company.

The adhesive composition comprises from about 0 to about 50 wt-%, preferably about 0.1 to about 10 wt-% and more preferably about 0.1 to about 5.0 wt-% of additives. Such additives include antioxidants, antiblock additives, pigments, filler and the like.

Antioxidants utilized herein include high molecular weight hindered phenol and multifunctional phenols such as sulfur and phosphorous containing phenols. Hindered phenols are well known in the art and may be characterized as phenolic compounds which also contain sterically bulky radicals in close proximity to phenolic hydroxyl group thereof. In particular, tertiary butyl groups generally are substituted onto the benzene ring in at least one of the ortho positions relative to phenolic hydroxyl group thereof. The presence of these sterically bulky substituted radicals in the vicinity of the hydroxyl group serves to retard its stretching frequency and correspondingly its reactivity, this steric hindrance thus providing the phenolic compound with its stabilizing

properties. Representative hindered phenols include 1,3,5 trimethyl 2,4,6-tris(3,5-ditert-butyl-4-hydroxybenzyl)benzene;pentaerythrityl tetrakis-3(3,5-di-tert-butyl-4-hydroxybenzyl)propionate; n-octadecyl-3 (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate; 4,4'-methylenbis(2,6-tert-butylphenol); 4,4'-thiobis(6-tert-butyl-o-cresol); 2,6-tert-butylphenol; 6-(4-hydroxyphenoxy)2,4-bis(n-octyl-thio)-1,3,5-triazine; di-n-octadecyl 3,5-ditert-butyl-4-hydroxy-benzylphosphonate; 2-(n-octylthio)ethyl 3,5-di-tert-butyl-4-hydroxy-benzoate and sorbitol hexa([3-(3,5-ditert-butyl-4-hydroxyphenyl)-propionate]. Commercially available antioxidants include Irganox[®]1010, Irganox[®]1076 and phosphites, Irgafos[®] 168, from Ciba Geigy.

10 The hot melt adhesives are suitable for application at a temperature of less than about 300°F (149°C), preferably less than about 275°F(135°C), more preferably about 250°F(121°C). A lower temperature is achievable by modifying the viscosity through polymer modification (higher MI and MFR). The viscosities are less than about 10,000 cPs at 150°C, more preferably about 10,000 cPs at 135°C, most preferably about 5,000 cPs at 121°C.

15 The hot melt adhesive of the present invention can be applied using techniques known to one of ordinary skill in the art such as the use of rollers or series of rollers, slot application and extrusion method.

20 Equipment contemplated for use in casemaking include existing equipments which have to be modified in accordance with the present invention include but are not limited to DA-Chronos casemaker and DA strato casemaker manufactured by Kolbus, Rahden, Germany; model RFC-101 roll fed casemaker manufactured by Crathern Engineering Co, Contoocook, New Hampshire, BDM casemaker Model 10,20,25 and 30 made by Horauf, Donzdorf, Germany; DM300 casemaker made by Stahl GmbH & Co., Ludwigsburg-Neckarweihingen, Germany; and Sheridan roll-fed casemakers. The equipment typically uses a one or two wheel glue pot application. The one wheel application may apply the adhesive or transfer the adhesive to another wheel which then applies the adhesive to the cover material and then applies the binder board to the coated cover material.

30 Puzzle and gameboards can be laminated utilizing the same or similar equipment as casemaking. Crather Spotter made by Crather Engineering Co may be used for this process.

Gluing off or thread securing is accomplished by using an extrusion system where a heated glue pot is utilized.

Tightbacking, lining up and sides or joint glue application are all accomplished by using equipments such as the Compact 2000 Model from Kolbus; equipment from
5 Stahl; and equipment from Freccia and Sheridan round backers are used for lining up.

Other than bookbinding, due to heat and UV light resistance, the adhesive compositions also find utility in a variety of "high performance" tape and label applications including tapes, tape applications for automobiles, eraser tapes, "hook and
10 loop" applications (Velcro®), labels for windows (automobile, boat and construction industries), labels for appliances and electronics, shelf marking adhesives and so forth.

All of the cited patents and publications are incorporated herein by reference. The following specific examples are provided to better assist the reader in the various aspects of practicing the present invention. As these specific examples are merely
15 illustrative, nothing in the following descriptions should be construed as limiting the invention in anyway.

EXAMPLES

Test Methods

Tensile and Elongation, Young's Modulus

20 Young's Modulus is a method of ranking the relative flexibility of adhesive films. Tensile and Elongation, Yield Point, and Young's Modulus are determined using ASTMD-638. The die used is an ASTMD-638 Type 4 die. A one inch gauge with a video extensometer is used to monitor elongation. The strain rate used is 25.4
cm/minute. The film thickness used is 20-25 mils. The resistance to tensile deformation
25 is measured at small strains.

The Tensile & Elongation was measured by first preparing a 2030 mil (0.5-0.7 mm) thick adhesive film free of air bubbles. Cut dogbones lengthwise from the film measuring the thickness at the gauge section (4mm±1.5mm). Condition the samples for at least 24 hours at 21°C and 23 to 50 percent relative humidity. Place each sample
30 in the jaws of an Instron tensile tester or equivalent with a load cell capable of measuring a 4 pounds (1.8kg) force +/- 1 percent. Elongate samples crosshead speed of 100 mm/minute until break. Record the "Ultimate Tensile" at yield by dividing the

maximum force by the cross-section area of the sample and $^{110}/_{10}$ Elongation" by dividing the displacement at break by the sample length and multiply by 100. The "Ultimate Tensile" and $^{110}/_{10}$ Elongation " are an average of three to five samples.

5 Peel And Shear

Peel and shear values were determined by placing samples in a programmed oven with a 100 g weight used for the peel mode and a 500 g weight used for the shear mode, and ramping the temperature up from about 25°C to 175°C at 25°C /hour. The oven automatically recorded the temperature at which the samples failed. Each sample was
10 coated onto kraft paper by hand using glass rods or shims. The resultant coating is a one inch wide band that is about 8-10 mils or about 0.02 cm to about 0.03 cm thick. Four to five bonds were made for the peel mode and four to five bonds were made for the shear mode and the results were averaged.

15 Cold Crack

Prepare several 1 inch by 3 inch (2.5 cm by 7.6 cm) adhesive films free of air bubbles which have a thickness of 20-30 mils (0.5 to 0.7 mm). Place three films individually over the "V" shaped base of a cold crack apparatus which consists of a stand with interlocking pressure bar. The stand is 3 inches (7.6 cm) by 0.75 inch (1.9 cm) wide
20 and 12 inches (30 cm) long. A 90° angle is cut squarely ½ inch (1.3 cm) deep into the top surface. The pressure bar, which is also cut at a 90° angle was placed into the gap of the stand. The test is repeated by lowering the temperature at 5° (3°C) increments with a new film sample for each temperature until the film cracks. If the film was cracked, the temperature was noted and the temperature was raised and the test repeated. If the film
25 did not crack, the temperature was lowered and the test was repeated to determine the lowest temperature at which cracking occurred. The recorded "cold crack" is an average of at least two samples.

Melt Viscosity

30 The melt viscosity of the hot melt adhesives were determined on a Brookfield Thermosel Viscometer Model using a number 27 spindle. The adhesive sample was melted in the thermosel at the temperature at which the viscosity was to be measured.

The spindle was lowered into the melted adhesive sample. The motor was turned on at the lowest speed and the corresponding torque reading displayed. The speed was increased until the torque reading stabilized and the viscosity measurement recorded after 30 minutes.

5

Bonding Tests

Bonds were prepared by extruding an adhesive bead onto the substrates using a Slautterback Mini-Squirt hand held, bench top applicator. The application temperature was about 170°C to about 200°C. The second substrate was immediately mated to the first and a 100 g weight was then rolled over the length of the bond line. The adhesive bead was maintained at approximately 8 inches with a weight of 1 gram. Bonds were allowed to age at ambient conditions for 24 hours and then torn apart by hand to determine if there was fiber tear or delamination.

15 The Mettler Ring and Ball Softening Points

The Mettler Ring and Ball Softening Points are determined using test method ASTM D-3461. The Ring and Ball Softening Point was determined with a Herzog MC 753 instrument. The rings were preheated to the melt temperature and then placed on release paper. The melted adhesive sample was then poured into the rings without inclusion of air bubbles. After cooling, excess adhesive was removed from the rings and two samples placed in the holder of the apparatus with a steel balls on top of each sample. The samples were lowered into a glycerin filled beaker positioned on a heating plate. The samples were lowered into the glycerin and heated at a rated of 5°C per minute. The average temperature at which the balls have fallen is recorded, the difference being not more than 1°C.

Example 1

Example 1-A describes a hot melt adhesive that is part of the present invention.

40-grams of Polymer A, an ethylene/ α -olefin interpolymer (0.87 g/cm³ density and 500 g/10 min melt index) was blended with 20-grams of paraffin wax, 39.5-grams Escorez[®] 5340 and 0.5-gram Irganox[®], to form a hot melt adhesive having a viscosity of 1045 cPs at a temperature of 350°F. The 100 g peel and cold crack are 128°F and 15°F.

Example 1-B describes a hot melt adhesive that is not part of the present invention.

Example 1-B was run exactly as described in Example 1-A with the exception that ethylene vinyl acetate was used as the base polymer. The hot melt adhesive had a viscosity of 1140 cPs at a temperature of 350°F. The 100 g peel and cold crack are
5 133°F and 35°F respectively.

Example 2

Example 2 describes a hot melt adhesive that is part of the present invention.

40-grams of Polymer A, an ethylene/ α -olefin interpolymers (0.87 g/cm³ density
10 and 500 g/10 min melt index) was blended with 20-grams of paraffin wax, 24.5-grams
Escorez[®] 5340, 15-grams of Escorez[®] 5400, and 0.5-gram Irganox[®], to form a hot melt
adhesive having a viscosity of 4930 cPs at a temperature of 350°F. The 100 g peel and
cold crack are 120°F and 5°F.

Example 3

Example 3 describes a hot melt adhesive that is part of the present invention.

20-grams of Polymer B, an ethylene/ α -olefin interpolymers (0.87 g/cm³ density
and 1000 g/10 min melt index) was blended with 15 grams KRATON[®] G-1730, 25-
grams of paraffin wax, 25-grams Escorez[®] 5340, 14.5-grams of Escorez[®] 5400, and 0.5-
20 gram Irganox[®], to form a hot melt adhesive having a viscosity of 2640 cPs at a
temperature of 350°F. The 100 g peel and cold crack are 122°F and 10°F respectively.

Example 4

Example 4 describes a hot melt adhesive that is part of the present invention.

25 20-grams of Polymer B, an ethylene/ α -olefin interpolymers (0.87 g/cm³ density
and 1000 g/10 min melt index) was blended with 15 grams KRATON[®] G-1657, 25-
grams of paraffin wax, 15-grams Escorez[®] 5340, 24.5-grams of Regalite[®] V-1120 and
0.5-gram Irganox[®], to form a hot melt adhesive having a viscosity of 2640 cPs at a
temperature of 350°F. The 100 g peel and cold crack are 122°F and 10°F respectively.

30

Example 5

Example 5 describes a hot melt adhesive that is part of the present invention.

8-grams of KRATON® G-1657 was blended with 33.5-grams Polymer B, an ethylene/ α -olefin interpolymers (0.87 g/cm³ density and 1000 g/10 min melt index), 35-grams of a blend of 1:1 ECR 158 and Escorez® 5615, 22-grams of Benzoflex® and 0.5-gram Irganox® to form a hot melt adhesive having a viscosity of 9040 cPs at a temperature of 275°F. The 100 g peel and cold crack are 130°F and 15°F respectively.

Example 6

Example 6 describes a hot melt adhesive that is part of the present invention.

8-grams of KRATON G-1730 was blended with 34-grams Polymer B, an ethylene/ α -olefin interpolymers (0.87 g/cm³ density and 1000 g/10 min melt index), 33.5-grams of a blend of 1:1 ECR 158 and Escorez® 5615, 23-grams of Benzoflex® 352 and 0.5-gram Irganox® to form a hot melt adhesive having a viscosity of 5375 cPs at a temperature of 275°F. The 100 g peel and cold crack are 136°F and 20°F respectively.

Example 7

Example 7 describes a hot melt adhesive that is part of the present invention.

8-grams of KRATON G-1657 was blended with 35-grams Polymer B, an ethylene/ α -olefin interpolymers (0.87 g/cm³ density and 1000 g/10 min melt index), 37-grams of a blend of 1:1 ECR 158 and Excorez® 5615, 20-grams of Benzoflex® 352 and 0.5-gram Irganox® to form a hot melt adhesive having a viscosity of 7250 cPs at a temperature of 275°F. The 100 g peel and cold crack are 127°F and 20°F respectively.

Example 8

Example 8 describes a hot melt adhesive that is part of the present invention.

40-grams Polymer B, an ethylene/ α -olefin interpolymers (0.87 g/cm³ density and 1000 g/10 min melt index), was blended with 23-grams of Benzoflex® 352, 35.5-grams of Escorez® 5615 and 0.5-gram Irganox®, to form a hot melt adhesive having a viscosity of 2060 cPs at a temperature of 275°F. The 100 g peel and cold crack are 120°F and 25°F respectively.

Table I Comparison of viscosity, peel and cold crack of Adhesive Formulation

Components	Example 1	Example 2	Example 3	Example 4	Comparative EVA based Example
PolymerA	40	40			
Polymer B			20	21	
155 Paraffin wax	20	20	25		
KratonG 1730			15		
KratonG 1657				14	
Escorez 5340	39.5	24.5	25.0	15	
Escorez 5400		15.0	14.5 Foral Ax		
Regalite V-1120				24.5	
Irganox 1010	0.5	0.5	0.5	0.5	
Viscosity at 325°F 350°F (177°C)	1045 cps	990 cps	1210 cps	2190 cps	1140cps
Viscosity at 300°F 325°F (163°C)				3100 cps	
Viscosity at 275°F 300°F (149°C)	2160 cps	2020 cps	2640 cps	4600 cps	2250 cps
Viscosity at 250°F 275°F (135°C)				7065 cps	3610 cps
Viscosity at 325°F 250°F (121°C)	5430 cps	4930 cps	7340 cps	11570 cps	6265 cps
100 g peel	128°F (53°C)	120°F (49°C)	122°F (50°C)	129°F (50°C)	133°F (56°C)
Cold Crack	1.5°F (-9°C)	5°F (-15°C)	10°F (-12°C)	10°F (-12°C)	35°F (2°C)

SUBSTITUTE SHEET (RULE 26)

Table II Comparison of Properties of Adhesive Formulation

Components	Example 5	Example 6	Example 7	Example 8
Block copolymer D		8		
Block copolymer E	8		6	
Polymer B	33.5	34	35	40
1:1 Blend ECR-158 & Escorez 5615	35	33.5	37	
Benzoflex	22	23	20	23
Irganox	0.5	0.5	0.5	0.5
Escorez 5340				35.5
Viscosity at 250°F (135°C)	9040 cps	5375 cps	7250 cps	
Viscosity at 300°F (149°C)	5360 cps	3040 cps	4310 cps	2060 cps
Viscosity at 350°F (177°C)	2240 cps	1870 cps	1870 cps	
100 g peel	130°F (54°C)	136°F (58°C)	127°F (53°C)	120°F (49°C)
500 g shear	152°F (67°C)	148°F (64°C)	150°F (66°C)	150°F (66°C)
Cold Crack	15°F (-9°C)	20°F (-7°C)	20°F (-7°C)	25°F (-4°C)
M Gardner	2	2	2	2

5

10

The above examples have been depicted solely for the purpose of exemplification and are not intended to restrict the scope or embodiments of the invention. The invention is further illustrated with reference to the claims that follow thereto.

What is Claimed is:

1. A hot melt adhesive for use in bookbinding comprising:
 - a) at least one homogeneous linear or substantially linear ethylene/ α -olefin
interpolymer;
 - b) optionally, at least one block copolymer;
 - c) at least one tackifying resin;
 - d) optionally, at least one plasticizer; and
 - e) optionally, at least one wax
2. The hot melt adhesive according to Claim 1 further comprising at least one additive.
3. The hot melt adhesive according to Claim 1 wherein the interpolymer has a density of from 0.850 to 0.885 g/cm³.
4. The hot melt adhesive according to Claim 1 or 3 wherein the interpolymer has a number average molecular weight (Mw) of greater than 20,000.
5. The hot melt adhesive according to Claim 1 or 3 wherein the interpolymer is an interpolymer of ethylene and C₃-C₂₀ α -olefin.
6. The hot melt adhesive according to Claim 5 wherein the C₃-C₂₀ α -olefin interpolymer is selected from the group consisting of propylene, isobutylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 4-methyl-1-pentene and 1-octene.
7. The hot melt adhesive according to Claim 1 or 3 wherein the block copolymer is selected from the group consisting of A-B-A triblock structures, A-B di-block structures, (A-B)_n radial block copolymer structures and graft or branched structures thereof.
8. The hot melt adhesive according to Claim 7 wherein the A component is a nonelastomeric styrene and the B component is elastomeric butadiene or hydrogenated/partially hydrogenated butadiene and the copolymer contains at least about 15% to about 40% styrene content.
9. The hot melt adhesive according to Claim 7 wherein the molecular weight of the block copolymer is about 50,000 to about 150,000.
10. The hot melt adhesive according to Claim 2 comprising:

- a) from about 5 to about 50-wt% of at least one homogeneous linear or substantially linear interpolpolymer;
 - b) optionally, from about 5 to about 50 wt-% of at least one block copolymer;
 - 5 c) from about 30 to about 80 wt-% of at least one tackifying resin;
 - d) optionally, from about 5 to about 55 wt-% of at least one plasticizer; and
 - e) from about 0 to about 50 wt-% of at least one additive and/or wax.
11. A method of binding books, comprising the steps of:
- 10 a) applying a film of a hot melt adhesive to a plurality of sheets at the backbone of a bookblock at a suitable temperature, said adhesive comprising:
 - i) at least one homogeneous linear or substantially linear ethylene/ α -olefin interpolpolymer;
 - 15 ii) optionally, at least one block copolymer;
 - iii) at least one tackifying resin;
 - iv) optionally, at least one plasticizer, and
 - v) optionally, at least one additive and/or wax;
 - b) laminating the sheets to the inside of the outer covering of the book;
 - c) allowing the film to solidify.
- 20 12. The method according to Claim 11, wherein the viscosity of the hot melt adhesive is less than 10,000 cPs.
13. The method according to Claim 11 or 13, wherein said adhesive is applied using a method selected from the group consisting of slot application, extrusion and use of roller.
- 25 14. A method for lining hard bound book blocks comprising the steps of:
- a) applying a molten film of hot melt adhesive to the bound edges of a book block;
 - b) applying thereto a scrim;
 - c) applying a second molten film of hot melt adhesive, and
 - 30 d) affixing thereto a strip of kraft paper in registered relation to the book spine, said hot melt adhesive comprising.

- i) at least one homogeneous linear or substantially linear ethylene/ α -olefin interpolymers;
 - ii) optionally, at least one block copolymer;
 - iii) at least one tackifying resin, and
 - 5 iv) optionally, at least one plasticizer;
 - v) optionally, at least one additive and/or wax.
15. A method for lining hard bound book blocks comprising the steps of:
- a) applying a molten film of hot melt adhesive according to Claim 1, 3 or 10 to the bound edges of a book block;
 - 10 b) optionally, applying capping paper over the molten hot melt adhesive;
 - c) applying a second molten film of hot melt adhesive;
 - d) applying thereto a scrim;
 - e) applying a third molten film of hot melt adhesive, and
 - 15 f) affixing a strip of kraft paper in registered relation to the book spine.
16. A method of using a hot melt adhesive for casemaking comprising the steps of:
- a) applying the hot melt adhesive according to Claim 1, 3 or 10 to the outer covering material of the book;
 - 20 b) placing book binder boards onto the outer covering material, and
 - c) laminating the outer covering material to the binder boards.
17. A method of using a hot melt adhesive for casing-in comprising the steps of:
- a) applying the hot melt adhesive according to Claim 1, 3 or 10 to the end sheets of a book block, and
 - 25 b) laminating the end sheets to the inside of the book cover case.
18. A method of using a hot melt adhesive for gluing-off or thread-securing, comprising the steps of:
- a) sewing a book or booklet together through the spine of the book or booklet using thread;
 - 30 b) extruding the hot melt adhesive according to Claim 1, 3 or 10 unto the spine of the book or booklet substantially covering the threads, and

- c) applying the book or booklet case to the spine of the book or booklet, wherein the hot melt adhesive is between the case and the spine of the book or booklet.

19. A case or cover for hard bound book comprising:

5

- a) an outer covering material, and
- b) book binder boards bonded to the outer covering material with the hot melt adhesive according to Claim 1, 3 or 10.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/30365

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09J123/16 B42C9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09J B42C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 00 00565 A (FULLER H B LICENSING FINANC ;DOW CHEMICAL CO (US)) 6 January 2000 (2000-01-06) page 38, line 20 -page 39, line 12; examples 32,33	1-19
X	WO 97 33921 A (FINLAYSON MALCOLM F ;FULLER H B LICENSING FINANC (US); KAUFFMAN TH) 18 September 1997 (1997-09-18) example 55; tables 16A,B	1-19

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

6 February 2001

Date of mailing of the international search report

01/03/2001

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schmidt, H

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/30365

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0000565 A	06-01-2000	AU 4728399 A	17-01-2000
WO 9733921 A	18-09-1997	AU 2213997 A	01-10-1997
		BR 9707995 A	27-07-1999
		CA 2248934 A	18-09-1997
		CN 1216552 A	12-05-1999
		EP 0886656 A	30-12-1998
		JP 2000507283 T	13-06-2000
		NO 984208 A	11-11-1998
		US 6008262 A	28-12-1999
		US 6107430 A	22-08-2000